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Substitution of Y for Pr in PrMn2Ge2-The magnetism of Pr0.8Y0.2Mn2Ge2

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Abstract

Pr0.8Y0.2Mn2 Ge 2 is found to exhibit four magnetic transitions on decreasing the temperature from the paramagnetic region: (i) paramagnetism to intralayer antiferromagnetism (AFl) at TN intra; (ii) AFl to canted ferromagnetism (Fmc) at TC inter; (iii) Fmc to conical magnetic ordering of the Mn sublattice (Fmi) at Tcc; and (iv) Fmi(Mn) to Fmi(Mn) + F(Pr) at TC Pr. These changes in magnetic structure are discussed in terms of changes in the Mn-Mn separation distances caused by the unit cell contraction and by electronic effects due to replacement of 20% of Pr with Y.

Keywords

8y0, pr0, magnetism, 2mn2ge2, prmn2ge2, substitution, pr, y

Disciplines

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Substitution of Y for Pr in $PrMn_2Ge_2$—The magnetism of $Pr_{0.8}Y_{0.2}Mn_2Ge_2$

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$Pr_{0.8}Y_{0.2}Mn_2Ge_2$ is found to exhibit four magnetic transitions on decreasing the temperature from the paramagnetic region: (i) paramagnetism to intralayer antiferromagnetism (AFl) at T_N^{intra}; (ii) AFl to canted ferromagnetism (Fmc) at T_C^{inter}; (iii) Fmc to conical magnetic ordering of the Mn sublattice (Fmi) at T_{cc}; and (iv) Fmi(Mn) to Fmi(Mn) + F(Pr) at T_C^{Pr}. These changes in magnetic structure are discussed in terms of changes in the Mn-Mn separation distances caused by the unit cell contraction and by electronic effects due to replacement of 20% of Pr with Y. © *2013 American Institute of Physics*. [http://dx.doi.org/10.1063/1.4798622]

Studies of materials that exhibit a large magnetocaloric effect (MCE) and potential for applications in magnetic refrigeration are important as sustainable and environmentally friendly alternatives to current refrigeration technologies [e.g., Ref. 1]. The discovery of a giant MCE in $Gd_5(Si_2Ge_2)$ (Ref. 2) led to increased efforts in the search for materials with a large MCE. The tetragonal intermetallic compounds RT_2X_2 (R = rare-earth; T = transition metal, and X = Si or Ge), with a layered structure similar to that of the $Gd_5Si_2Ge_2$ system, exhibit a wide range of magnetic behaviours and have been studied extensively in the continuing searching for novel MCE materials.[3–5] Among them, $PrMn_2Ge_2$ and related compounds offer interesting prospects for enhanced magnetocaloric behaviour[6] as their layered structure allows control of the intrinsic magnetism of the Mn sublattice via inter-planar and intra-planar separations of the Mn atoms with the Pr atoms contributing to increased magnetization due to ferromagnetic coupling between the Mn and Pr sublattices below the Pr ordering temperature T^{Pr}_C.[6] Based on the smaller atomic radius of Y (=1.78 Å) compared with Pr (1.82 Å), substitution of Y for Pr in $PrMn_2Ge_2$ is expected to lead to a significant decrease in $d_{Mn–Mn}$ and a corresponding drastic modification of magnetic states.[7,8] Here, we outline the influence of substituting Pr with Y in $Pr_{1-x}Y_xMn_2Ge_2$ with x = 0.0–1.0 and present a detailed determination of the intrinsic magnetism of $Pr_{1-x}Y_xMn_2Ge_2$ with x = 0.2.

The $Pr_{1-x}Y_xMn_2Ge_2$ (with x = 0.0-1.0) samples were prepared by arc melting stoichiometric amounts of the pure elements and then sealed under vacuum in a quartz tube, annealed for 1 week at 900 °C, and quenched in water. Neutron diffraction experiments were carried out on the GEM time-of-flight diffractometer at ISIS (STFC, UK) from 30 to 360 K (Ref. 8) and the Echidna diffractometer at OPAL.

Cu-Kα x-ray diffraction confirmed that the $Pr_{1-x}Y_xMn_2Ge_2$ compounds crystallize in the tetragonal $ThCr_2Si_2$-structure and that the lattice parameters decrease as the Y concentration increases as expected, with the change in unit cell volume for $Pr_{1-x}Y_xMn_2Ge_2$ given by $dV/dx \sim -12.4$ Å^3 ($da/dx \sim -0.131$ Å and $dc/dx \sim -0.053$ Å). The overall magnetic behaviour of RMn_2Ge_2 compounds is strongly influenced by two critical intralayer Mn–Mn distances d^a_{Mn-Mn}: $d_{crit1} = 2.87$ Å and $d_{crit2} = 2.84$ Å.[3–6] It has been found that for $Pr_{1-x}Y_xMn_2Ge_2$ compounds the Mn–Mn intralayer distance $d^a_{Mn–Mn}$ decreases significantly with increasing Y content from 2.915 Å for x = 0 ($>d_{crit1}$) to 2.826 Å for x = 1.0 ($<d_{crit2}$). The decrease in $d^a_{Mn–Mn}$ is correspondingly accompanied with a change in the magnetic state at room temperature from ferromagnetism for $x < 0.7$ to antiferromagnetism for $x \geq 0.8$.[7,8] Refinement of the room temperature neutron diffraction pattern of $Pr_{0.8}Y_{0.2}Mn_2Ge_2$ yields the intralayer Mn–Mn spacing $d^a_{Mn-Mn} = 2.907$ Å $> d_{crit1} = 2.87$ Å.

The temperature dependence of the magnetization (H = 100 Oe; 10–340 K) and DSC results (300–600 K) for $Pr_{0.8}Y_{0.2}Mn_2Ge_2$ are shown as a composite figure in Fig. 1. Four magnetic transitions (rather than one as reported in Ref. 7) can be readily identified for $Pr_{0.8}Y_{0.2}Mn_2Ge_2$ with transition temperatures $T_N^{intra} = 375$ K, $T_C^{inter} = 335$ K, $T_{cc} = 245$ K, and $T_C^{Pr} = 42$ K as discussed below (the transition temperatures T_C^{inter}, T_N^{inter}, and T_C^{Pr} were defined as the temperatures at which dM/dT diverges[9]). The M-T data were measured in a field of 100 Oe over the temperature range of 10–340 K after cooling in zero field (the warming and cooling curves are marked by arrows) with magneto-history effects evident at $T_C^{inter} = 335$ K.[10] Magnetization measurements at 10 K, 50 K, and 250 K in fields up to 5 T yield a saturation magnetization of 45.0 emu/g (3.11 μ_B/f.u.), 38.2 emu/g (2.64 μ_B/f.u.), and 35.9 emu/g (2.48 μ_B/f.u.), respectively, indicating substantial FM order. Based on the analogous magnetic behaviour between $PrMn_2Ge_2$ (Ref. 3) and $Pr_{0.8}Y_{0.2}Mn_2Ge_2$ and the neutron refinements described below, in order of decreasing temperature, the four transition temperatures can be defined as T_N^{intra}, T_C^{inter}, T_{cc}, and T_C^{Pr}.

Fig. 2(a) shows a representative set of neutron diffraction patterns for $Pr_{0.8}Y_{0.2}Mn_2Ge_2$ at 10 K steps over the

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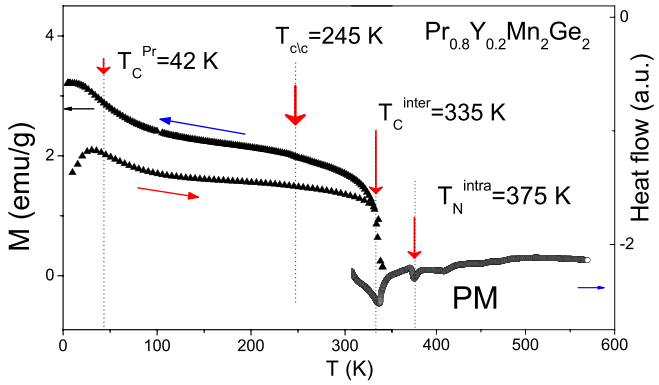

FIG. 1. Composite figure showing the temperature dependent magnetization obtained on cooling $Pr_{0.8}Y_{0.2}Mn_2Ge_2$ in a field of 100 Oe (left part; 10-340 K) and the differential scanning calorimetry results (right part; 300–600 K). The M-T curves show the results for warming and then cooling after first cooling from room temperature in zero field (transition temperatures indicated by arrows).

temperature range of 30–360 K. As described elsewhere [e.g., Ref. 3], the temperature dependences of the intensities of the (112), (101), and (103) peaks (Fig. 2(b)) correspond well with changes in magnetic states at T_C^{inter}, T_{cc}, and T_C^{Pr} as indicated by the magnetic studies (Fig. 1) as discussed above. Fig. 2(c) shows a series of neutron diffraction patterns and Rietveld refinements of $Pr_{0.8}Y_{0.2}Mn_2Ge_2$ at selected temperatures. These patterns exemplify the four different magnetic regions and structures encountered below $T_N^{intra} = 375$ K. Here, we describe the magnetic structures in terms of the notation outlined by Venturini *et al.*[10]

The first magnetic transition occurs around $T_N^{intra} \sim 375$ K. While we were unable to collect diffraction patterns above ~360 K during the experiments at ISIS,[8] refinements of the neutron patterns between 360 K and 335 K confirmed that the compound exhibits the AFl magnetic structure (this is reflected, for example, by the increase in the (101) peak intensity as in Figs. 2(a) and 2(b)). This allows us to ascribe the transition temperature $T_N^{intra} \sim 375$ K as originating from the transition from paramagnetism to intralayer antiferromagnetism (AF*l*).

The second transition at $T_C^{inter} \sim 335$ K is clearly reflected by enhancements of both the (112) and (101) peak as the temperature decreases (Figs. 2(a)–2(c)). This behaviour indicates the presence of components of the Mn moment below 335 K both within the ab-plane (AF order as reflected by the (101) peak) and along the c-axis (FM order as indicated by the (112) peak). It is therefore concluded that the transition at $T_C^{inter} = 335$ K reflects the change from the AF*l* magnetic structure to the canted ferromagnetic spin structure F*mc*.

The onset of satellite reflections $(101)^+$, $(101)^-$, $(103)^+$, and $(103)^-$ at $T_{cc} \sim 245$ K mark formation of the conical configuration Fmi magnetic state (see Figs. 2(a) and 2(c)). The Fmi structure represents the ferromagnetic mixed incommensurate structure characterised by ferromagnetic interplanar coupling of the in-plane ferromagnetic

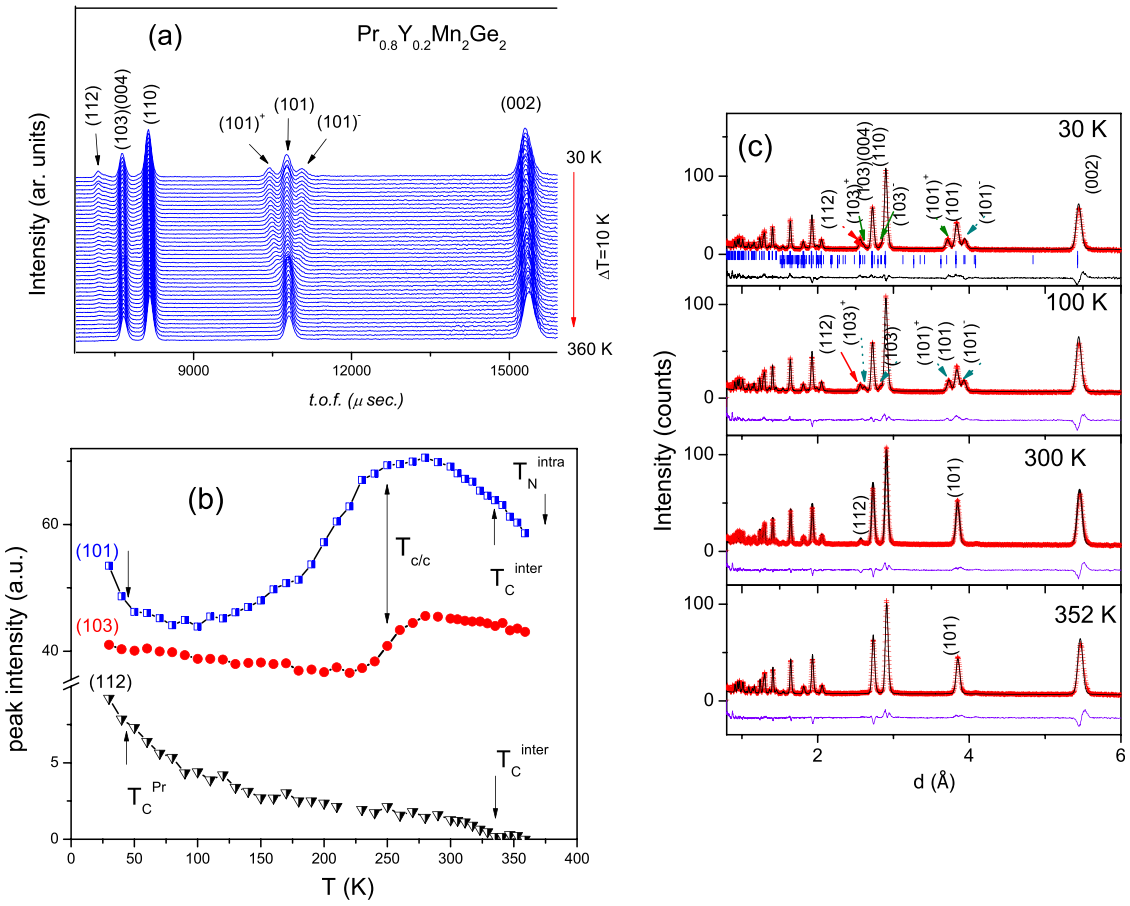

FIG. 2. (a) Representative neutron diffraction patterns for $Pr_{0.8}Y_{0.2}Mn_2Ge_2$ at 10 K intervals over the temperature range of 30–360 K (GEM, ISIS, STFC); (b) temperature dependences of the (101), (103), and (112) peak intensities; (c) neutron diffraction patterns of $Pr_{0.8}Y_{0.2}Mn_2Ge_2$ at 30 K, 100 K, 300 K, and 352 K. The full lines through the data represent the Rietveld refinements with the differences plot also shown for each pattern and refinement.

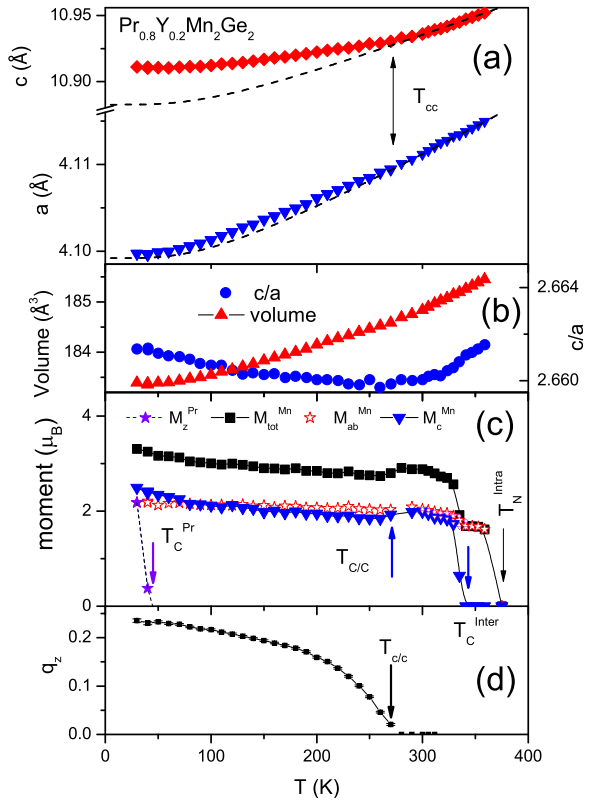

FIG. 3. Temperature dependences of structural and magnetic parameters for $Pr_{0.8}Y_{0.2}Mn_2Ge_2$ as derived from refinements of the neutron diffraction patterns. (a) Lattice parameters *a, c*; (b) unit cell volume *c/a*; (c) magnetic moment; (d) the q_z component of the wavevector. The dashed lines in Fig. 3(a) show the phonon contribution to the lattice expansion as evaluated from the Grüneisen relation.

components and by the incommensurate arrangement of the antiferromagnetic in-plane components. The component q_z of the wavevector dictates the phase difference between Mn spin along the screw axis **c** equal to $2\pi(0, 0, q_z)(0, 0, 1) = 2\pi q_z$.[3] The temperature dependence of the propagation vectors q_z has been derived from the Rietveld refinements and is presented in Fig. 3(d).

Further increases in the intensities of both the (112) and (101) peak are observed on cooling $Pr_{0.8}Y_{0.2}Mn_2Ge_2$ below $T_C^{Pr} \sim 42$ K (Fig. 2(b)). As supported by refinements of the neutron patterns, this additional magnetic scattering is due to ferromagnetic ordering of the Pr magnetic sublattice, F(Pr), leading to a combination of the F*mi* structure of Mn-sublattice and the ferromagnetic ordering of the Pr magnetic sublattice F(Pr) below $T_C^{Pr} \sim 42$ K. At 30 K, it has been derived that the Pr and Mn magnetic moments are 2.18 μ_B and 3.31 μ_B, respectively, with $q_z = 0.235$. The canting angle of Mn moments with respect to the *c*-axis at 30 K is derived to be 41.2°. Compared with q_z in $PrMn_2Ge_2$ compound ($q_z = 0.28$ at 2 K) and $Pr_{0.8}Lu_{0.2}Mn_2Ge_2$ ($q_z = 0.21$ at 3 K),[3] it can be seen that the replacement of the nonmagnetic elements Y or Lu for Pr leads to a decrease in q_z and that Lu is more effective than Y in modifying q_z.

The structural and magnetic moment values resulting from refinements of the variable temperature neutron diffraction data (~30-360 K) are shown in Fig. 3. The unit cell is found to exhibit an anisotropic change with increasing temperature (e.g., c/a versus T graph of Fig. 3(b)) with a pronounced magneto-volume effect evident (especially in the c-axis). The dashed lines in Fig. 3(a) show the phonon contribution to the lattice expansion as evaluated from the Grüneisen relation using a Debye temperature $\theta_D = 400$ K [see Ref. 4] and extrapolated from the paramagnetic region into the magnetically ordered region for comparison with the experimental lattice parameters.[11]

Compared with the transition temperatures reported for $PrMn_2Ge_2$ ($T_N^{intra} = 415$ K, $T_C^{inter} = 334$ K, $T_{cc} = 280$ K, and $T_C^{Pr} = 100$ K),[12] replacement of Pr with 20% of Y leads to a reduction in the transition temperatures (other than T_C^{inter} which remains essentially unchanged). Given that contraction of the unit cell volume due to Y substitution (chemical pressure) can be considered equivalent to the influence of external pressure, the corresponding chemical pressure can be derived to be 5.0 kbar for $Pr_{0.8}Y_{0.2}Mn_2Ge_2$ using the Murnaghan equation.[3] Using the values of $dT_C^{Pr}/dp = -5.8$ K/kbar for $Pr_{0.5}Y_{0.5}Mn_2Ge_2$ compound[13] and $dT_C^{inter}/dp = -0.2$ K/kbar for $PrMn_2Ge_2$,[14] the expected values of T_C^{Pr} and T_C^{Inter} due to the "chemical pressure" in $Pr_{0.8}Y_{0.2}Mn_2Ge_2$ should be $T_C^{Pr} = 71$ K and $T_C^{inter} = 333$ K. Compared with the experimental values of $T_C^{Pr} = 42$ K and $T_c^{inter} = 335$ K in $Pr_{0.8}Y_{0.2}Mn_2Ge_2$, it can be concluded that in addition to the geometric effects associated with the interplanar and intra-planar separation distances as discussed above, changes in the electronic configurations due to Y substitution for Pr as well as increase in the concentration of the nonmagnetic Y atoms, have a significant effect on the overall magnetic behaviour of $Pr_{0.8}Y_{0.2}Mn_2Ge_2$.

$Pr_{0.8}Y_{0.2}Mn_2Ge_2$ compound follows the sequence of magnetic structures with decreasing temperature: PM → AFl → Fmc → Fmi → Fmi + F(Pr). Replacement of Pr with 20% of Y leads to a reduction in the transition temperatures and the q_z propagation vector component compared with the behaviour shown by $PrMn_2Ge_2$.

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